ENABLING HIGH-ENERGY/HIGH-VOLTAGE LITHIUM-ION CELLS FOR TRANSPORTATION: PROJECT COMPLETION HIGHLIGHTS, PART 1

Project ID: BAT252

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Argonne National Laboratory

June 11, 2019

2019 DOE Vehicle Technologies Office Annual Merit Review

Overview

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2018
- Percent complete: 100%

Budget

- Total project funding:

  FY18 $4.0M
- BAT252, BAT253(ANL, NREL, ORNL, LBNL)

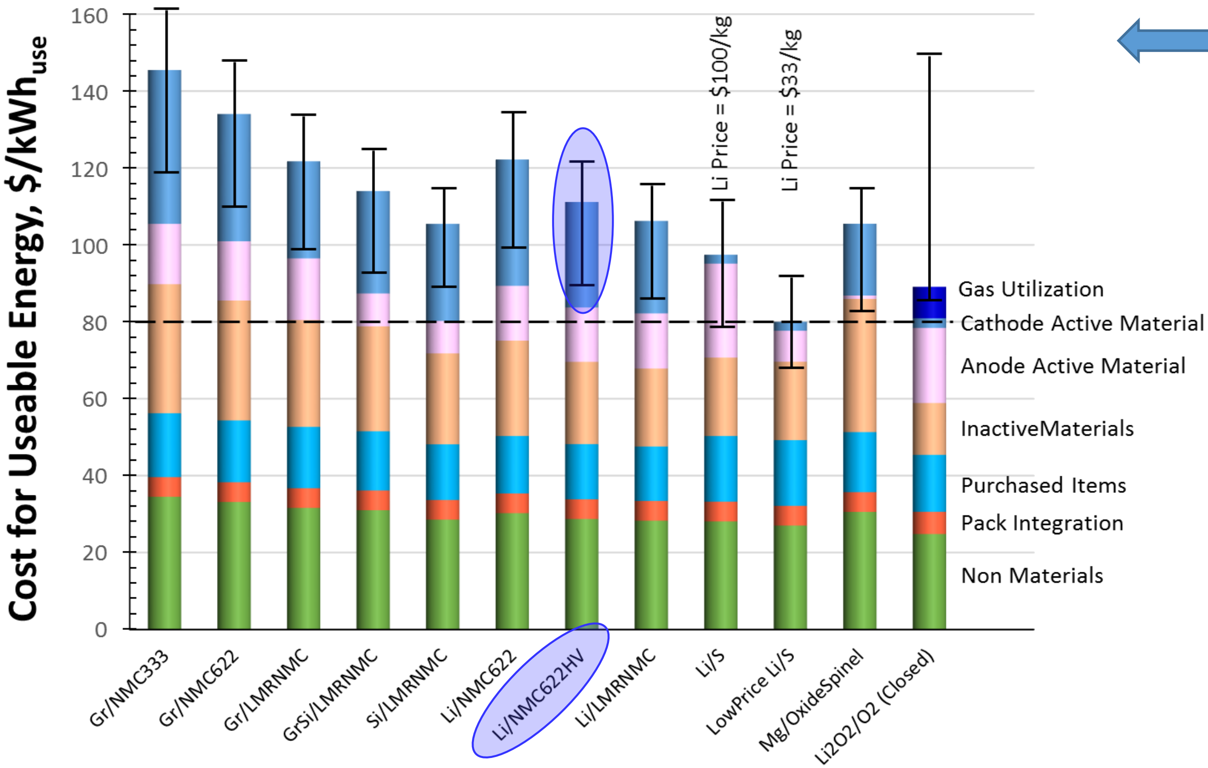
Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost
  - Performance
  - Safety

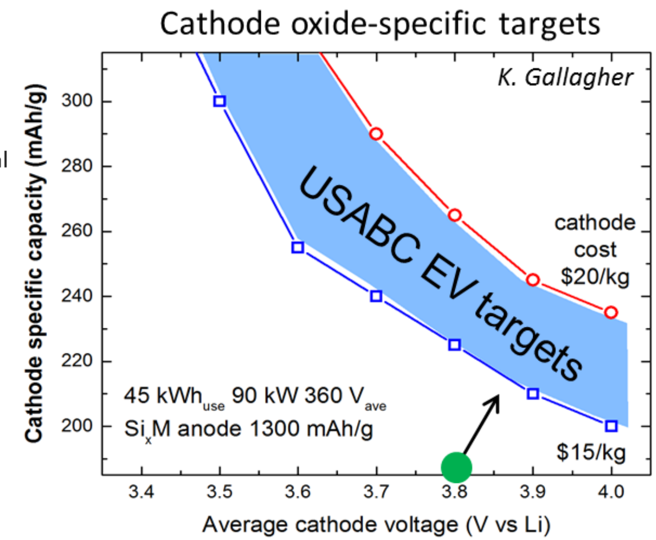
Partners

- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

Relevance



BatPaC Projected Cost for a 100kWh$_{Total}$, 80kW Battery Pack



- Traditional NMC-based, Li-ion cathodes, paired with advanced anodes, are still the best options for near-term advancements (~80-100 $/kWh$_{use}$)
- Increasing operating voltages greatly improves energy
- 'High-voltage' instabilities must be mitigated to take full advantage of NMCs

Milestones/Approach

Overall Objectives

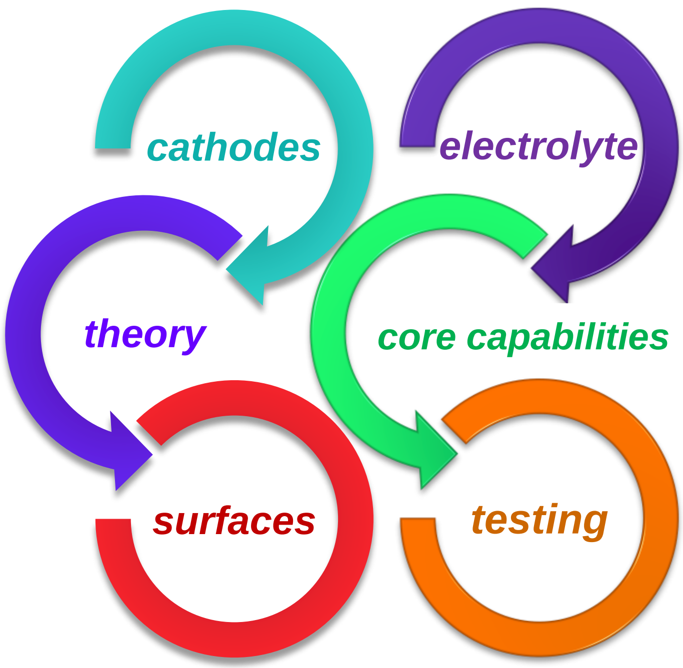
Enable high-energy lithium-ion cells through:

- *Identification of major challenges*
- *Understanding of high voltage processes*
- *Development of promising strategies via New materials*
- *Validation under protocols*

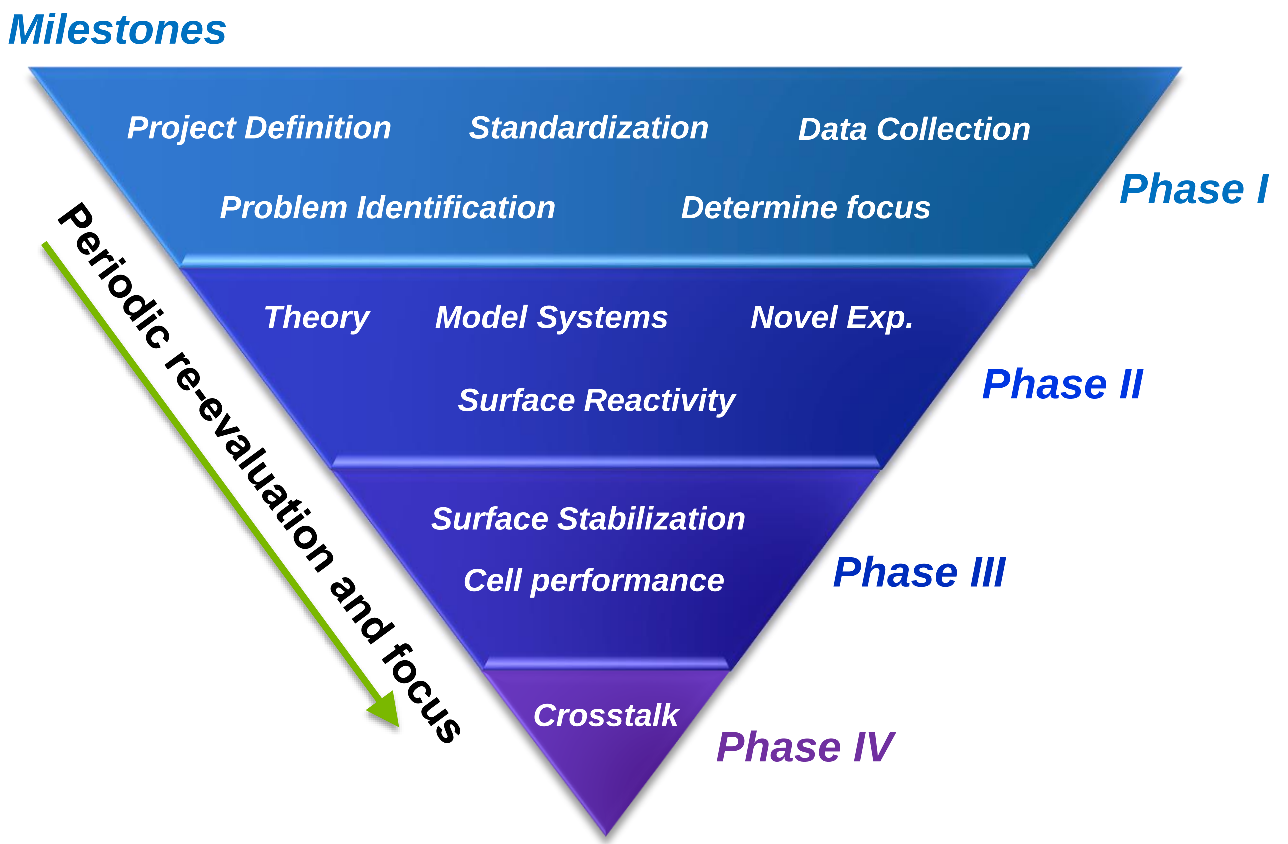
Project Management

- Sub-groups by expertise with defined cross collaborations (*'Sprints'*)
- Weekly, full-team meetings with research updates, discussions, and project info
- Periodic, full-team "reviews" to inform project focus
- Online database of all project data/protocols/info accessible to all team members

Project Thrusts



Milestones/Approach



Five Major Focused Projects

- *Standards and Protocols*
- *Development of Model Systems*
- *Electrolyte 'Sprint'*
- *Additives 'Sprint'*
- *Effort on Crosstalk*

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Milestones/Approach: *Standards and Protocols*

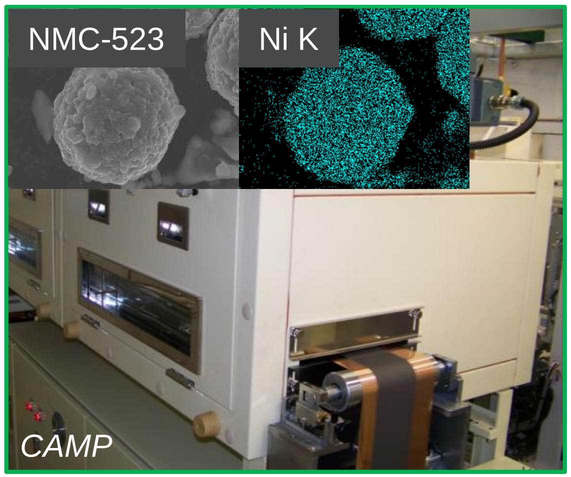
Materials and Electrodes

- Industrially prepared cathode materials
- CAMP prepared, matched electrodes
- Distributed project wide

Electrochemical

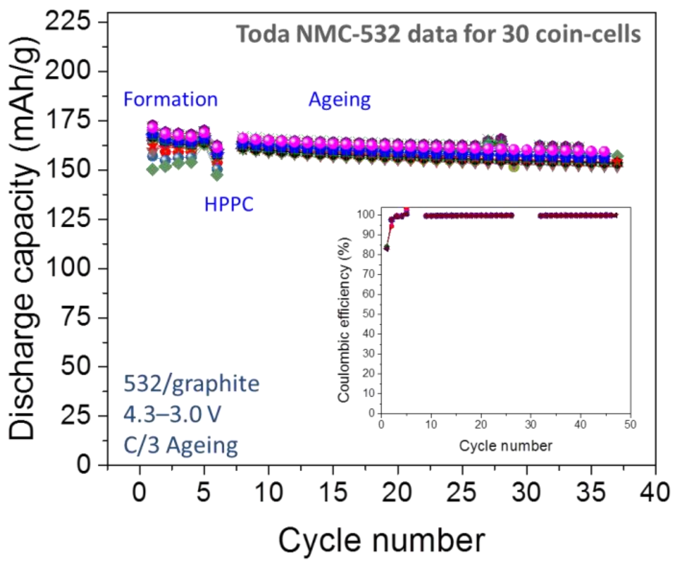
- How to make cells
- Standardized cycling protocols
- FOM evaluation
- HV stability (e.g., electrolyte O_x)
- Statistical analysis of multi-cell sets

Electrode Fabrication

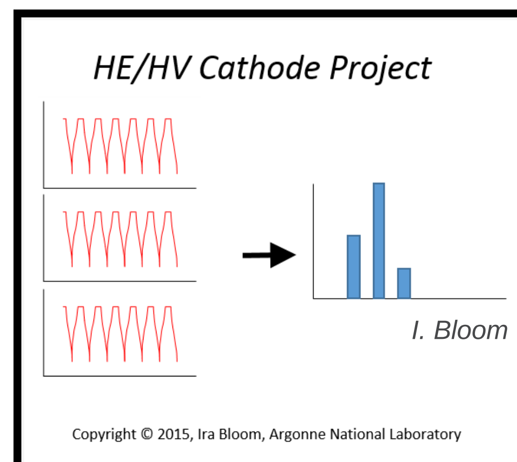


See also BAT253

Baselines/benchmarks

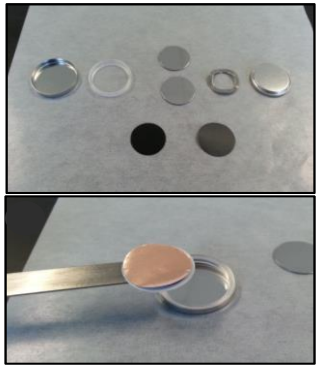


Data Analysis

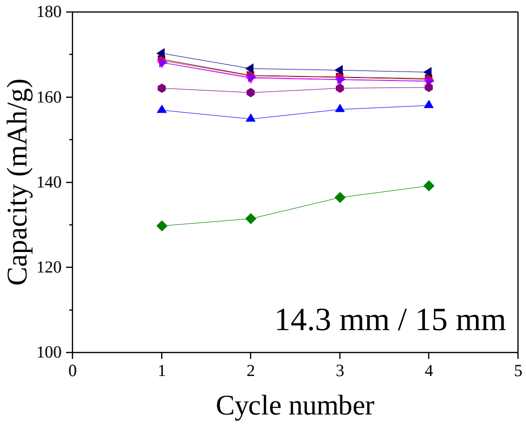


Progress: *Standards and Protocols*

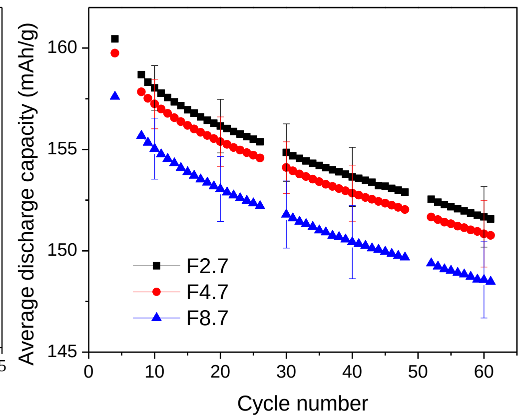
Cell assembly



Electrode sizing

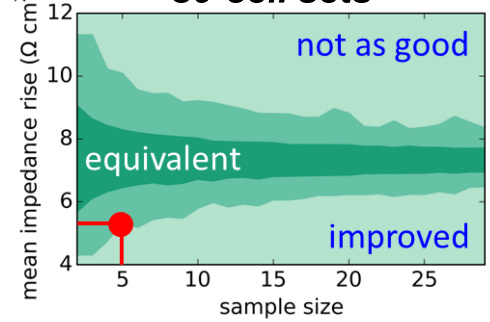


Electrolyte volume

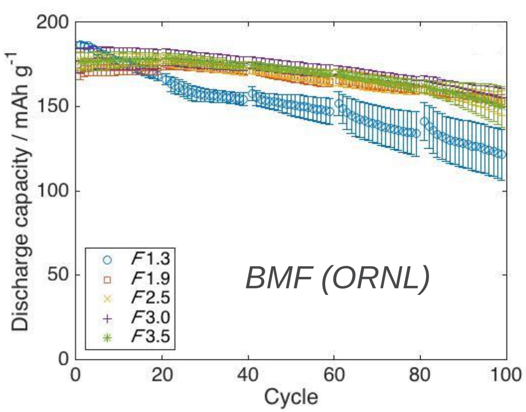


Statistical Analysis

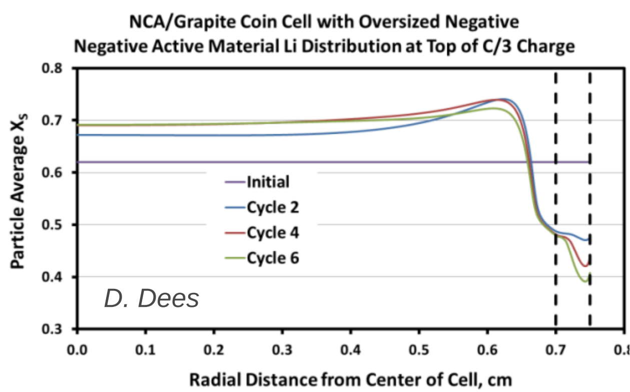
30-cell sets



Pouch/coin cell correlations



Electrochemical Modeling



All aspects of standardized testing have been studied and published

Enabling High-Energy, High-Voltage Lithium-Ion Cells: Standardization of Coin-Cell Assembly, Electrochemical Testing, and Evaluation of Full Cells
*B.R. Long et al., J. Electrochem. Soc., **163**, A2999 (2016)*

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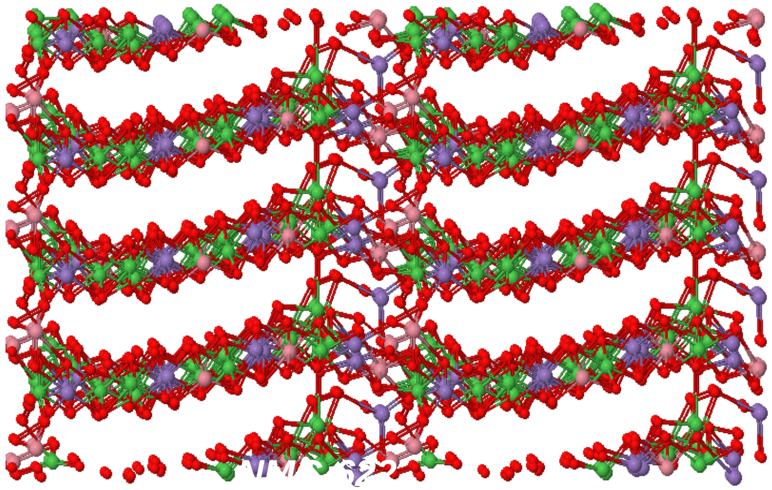
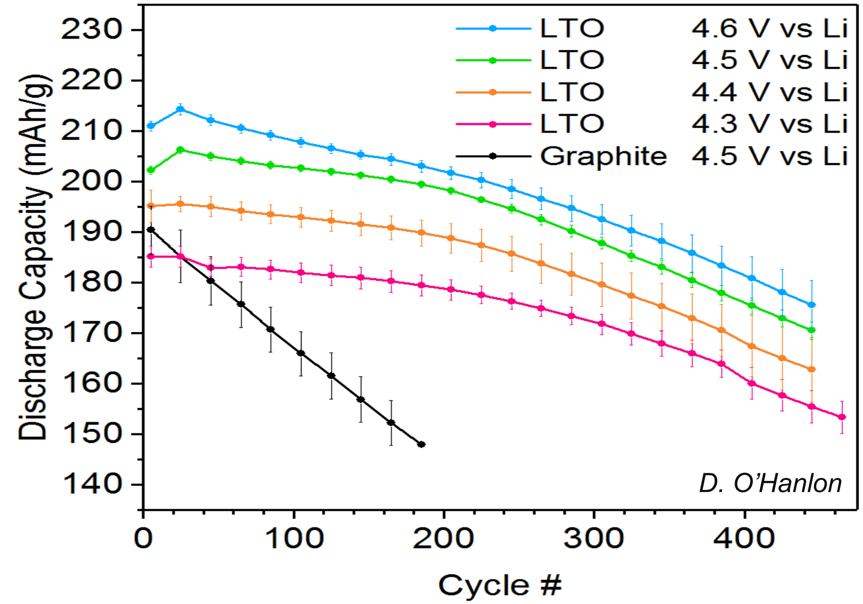
Progress: *Defining the Challenges*

Delithiated NMC-532 *H. Iddir*

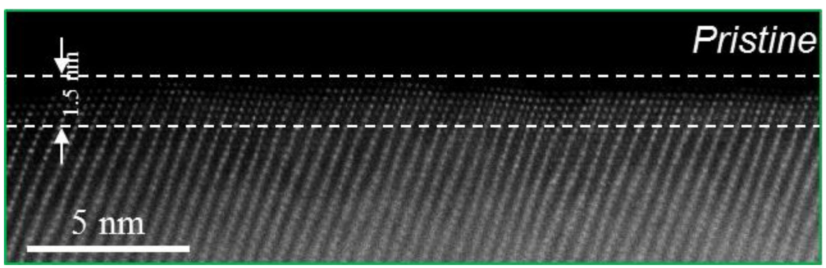


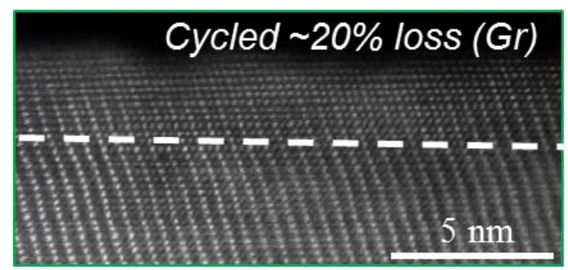
Theory predicts bulk structure remains intact up to ~ $Li_{0.25}MO_2$ (75% delithiation)



- NMC-622//LTO ~500 cycles (~20% loss)
- NMC-622//Gr ~180 cycles

S. Sharifi-Asl

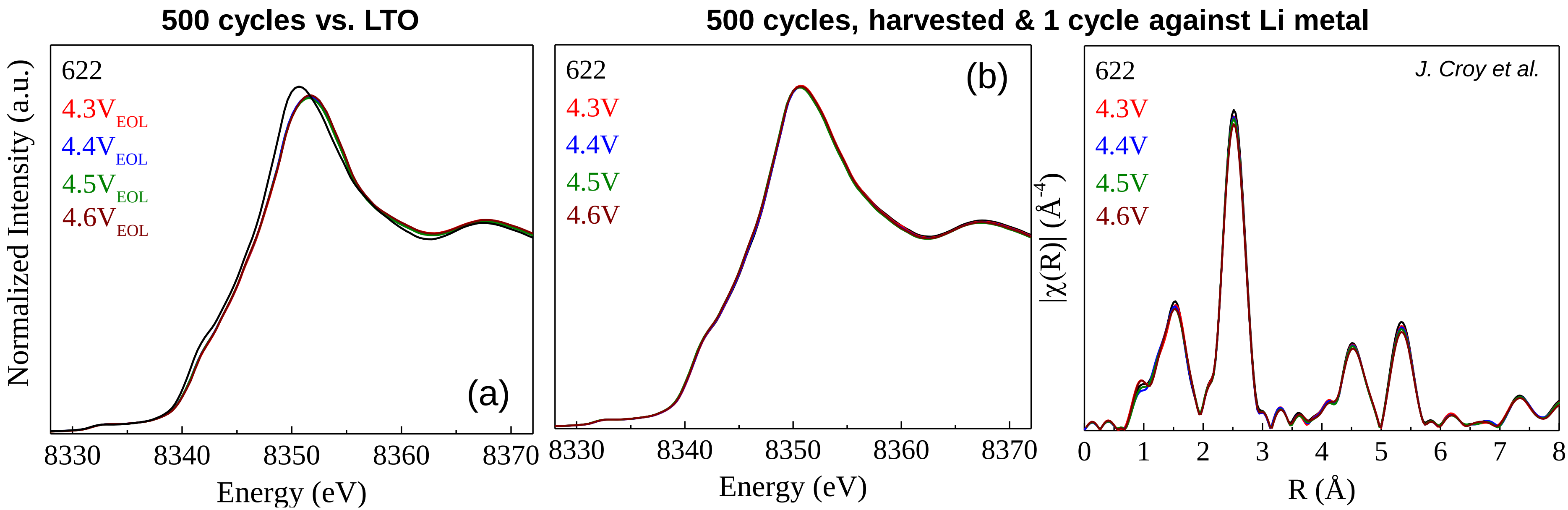




Pristine NMC-622 shows well-layered structure with ~1-2 nm surface reconstructions

Cycled 622 shows layered structure with ~3-4 nm reconstruction

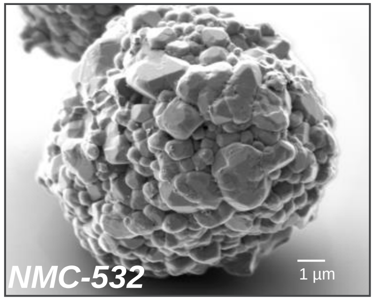
Progress: *Defining the Challenges*



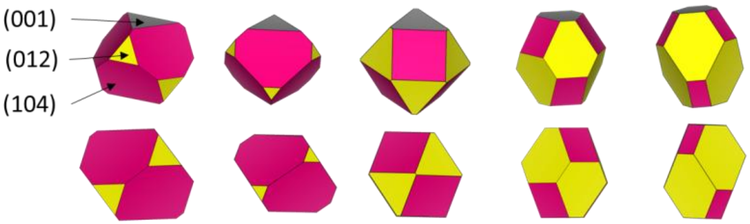
(a) Hard X-ray absorption (bulk average probe) shows shift in Ni edge after ~20% capacity loss (Li trapping at anode)

(b) Harvesting cathode and discharging against Li metal shows a fully recovered average structure after cycling at all voltages (High-res, diffraction gives concurring results)

Changes to the bulk structure of the NMC oxide are not the main contributor to cell degradation (~4.5V vs. Li) → Focus on surfaces



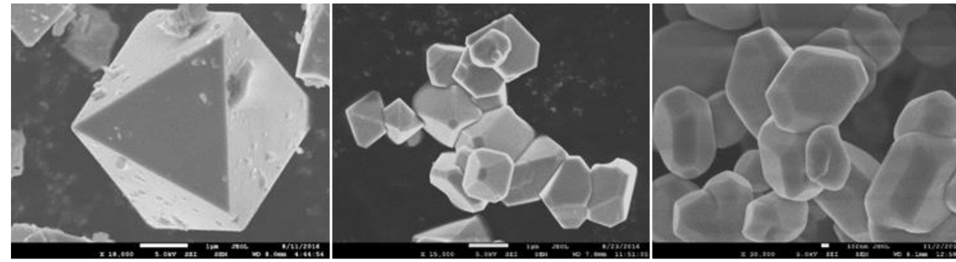
Progress: *Development of Model Systems*



H. Iddir et al.

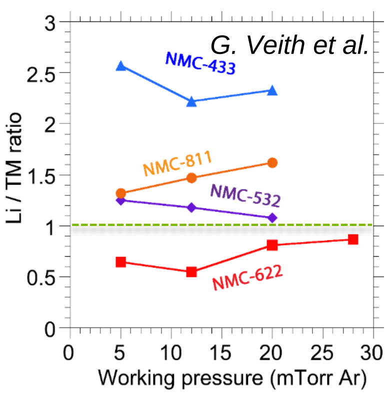
Theory & Modeling

Single-Crystal NMCs

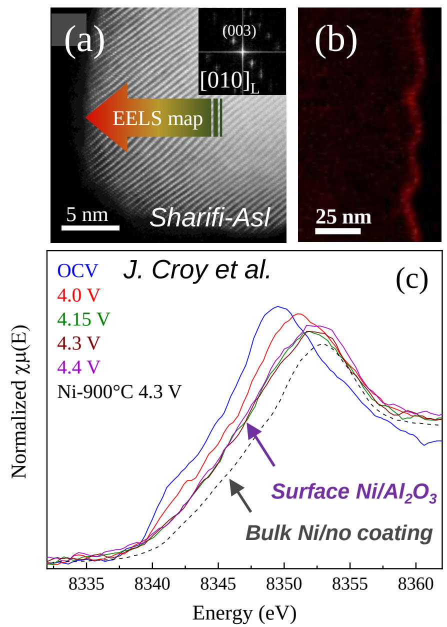


G. Chen et al.

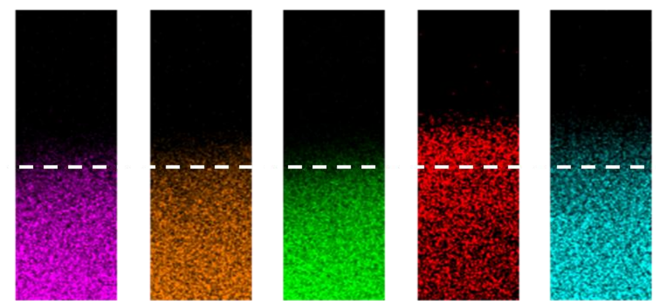
Thin-films



Modified NMCs

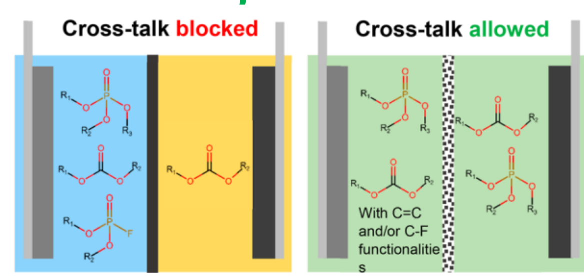


Model Coatings



B. Han et al.

Two-compartment Cells



Sahore,Vadivel et al.

Theory

Model Systems

Practice

Model systems with practical attributes

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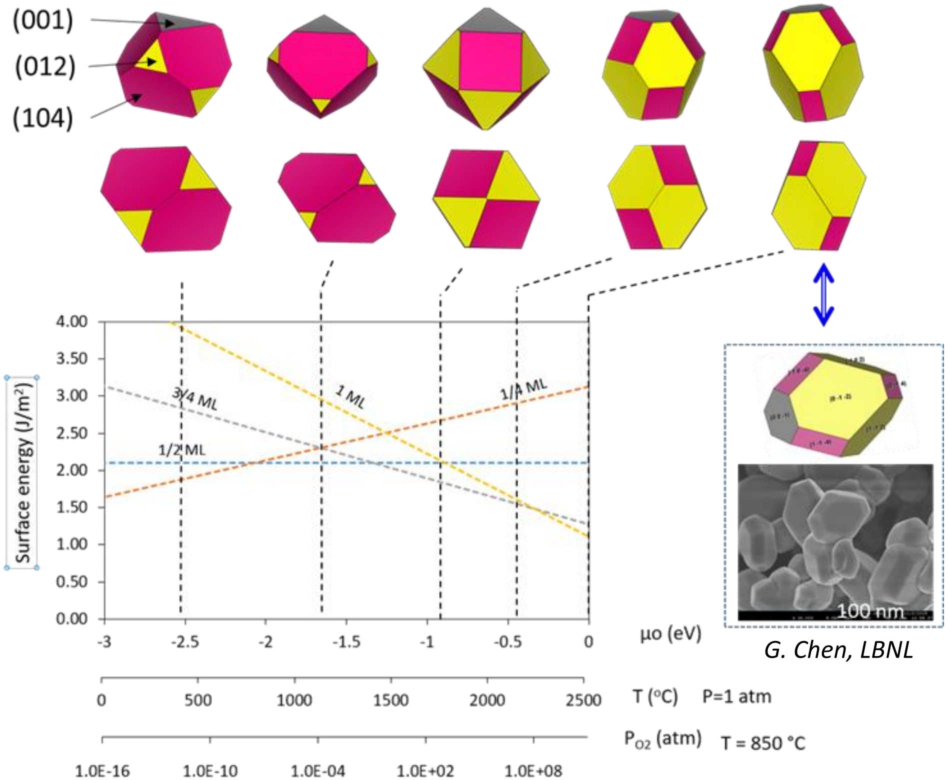
Progress: *Theory of NMC Surfaces and Interactions*

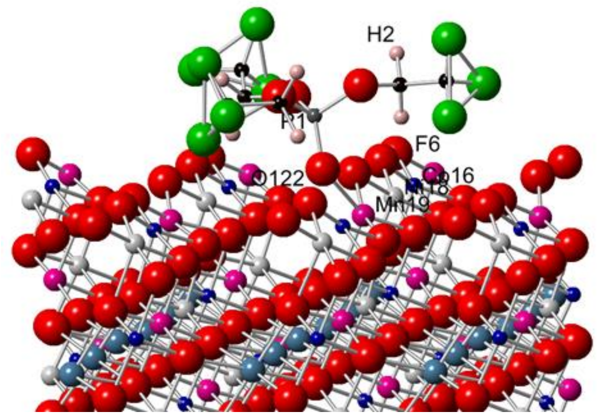
H. Iddir, J. Garcia

Predicting morphology of NMCs



G. Chen, LBNL

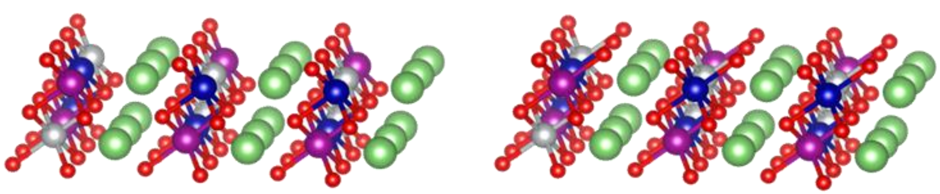
Additive interactions and design



Theory/modeling was used to study:

- Low-energy surfaces
- Surface terminations
- Particle morphologies
- Surface dependent reactivity
- Surface-dependent segregation
- Surface-dependent reconstruction

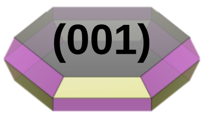
Predicting atomic structure of surfaces

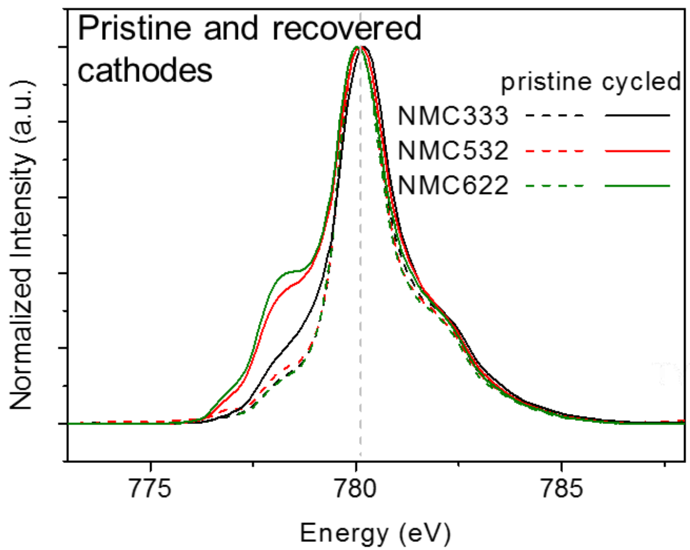


Computational foundation for atomistic modeling of NMCs completed

Progress: *Synthesis and Characterization of Single Crystal NMCs*

NMC-111
NMC-532
NMC-622

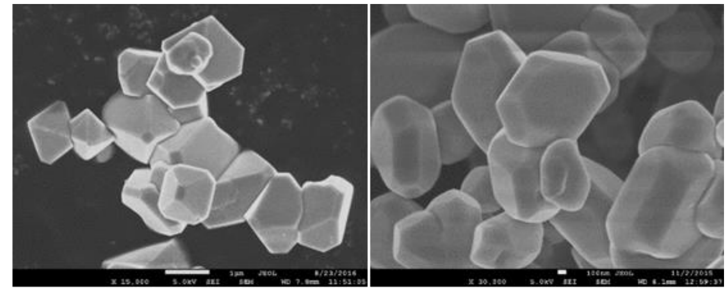




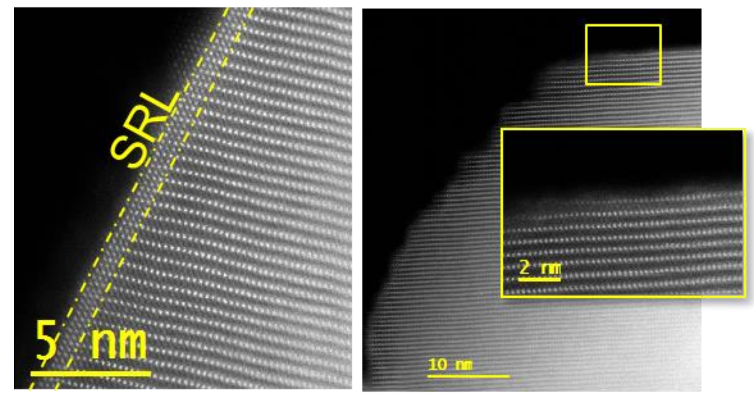
- Various compositions dominated by (001), cycled and recovered for L-edge XAS.
- Composition-dependent changes observed for particles with similar facating

NMCs exhibit facet/composition-dependent properties, single crystals allow more direct comparison of theory & experiment

G. Chen et al.



R. Shahbazian-Yassar, S. Sharifi-Asl



- Typical surface reconstruction layer (SRL) on pristine NMC-111 is ~1 nm.
- Formation of SRL facet dependent – no SRL seen on pristine (001) surface of NMC-111.

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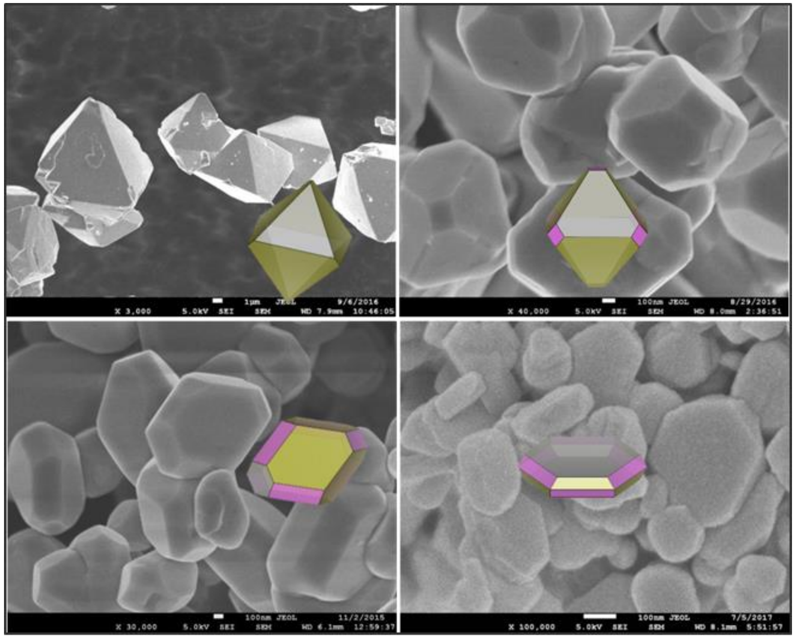
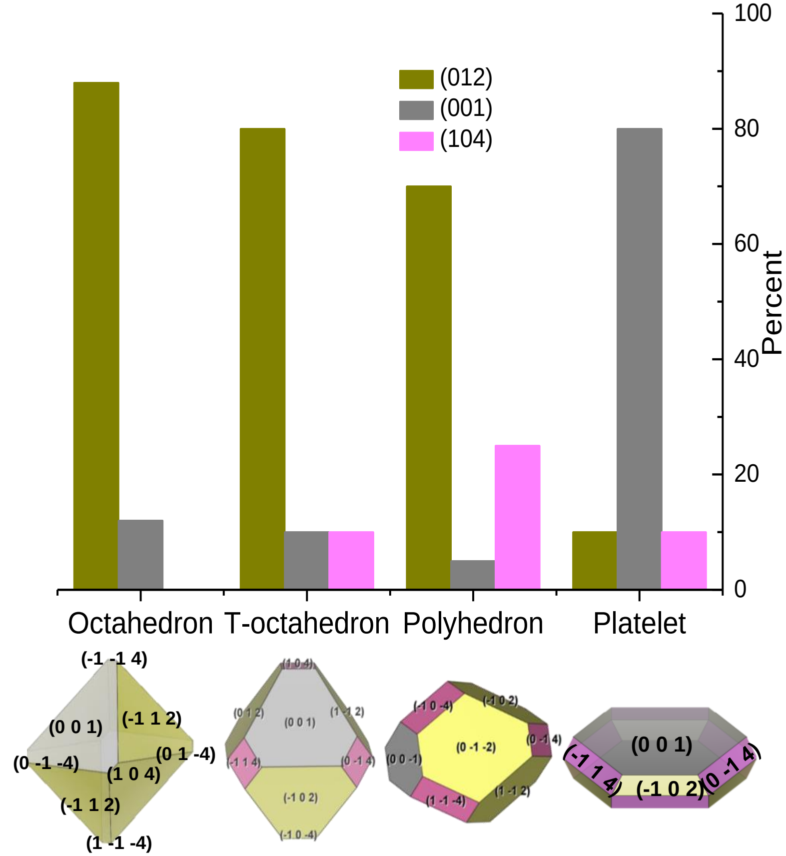
Progress: *Correlating Models, Theory and Experiment*



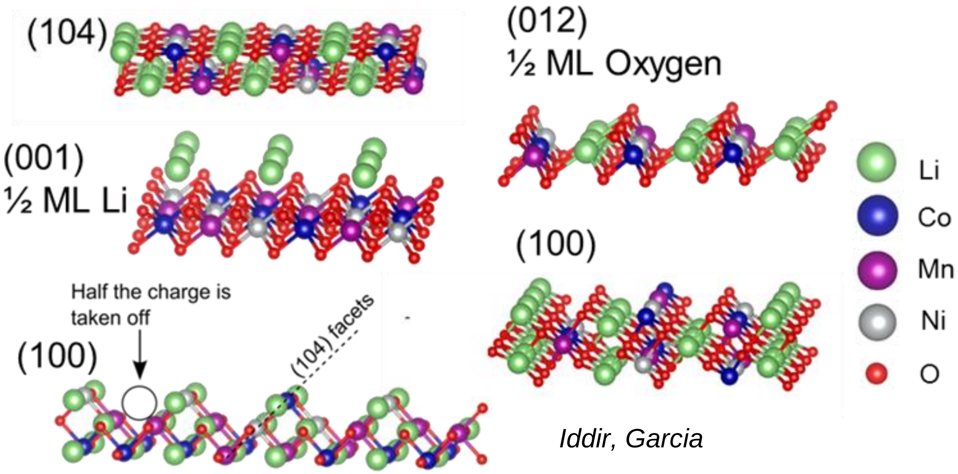
J. Zhu et al. *J. Mater. Chem. A* **2019,** *7*, 5463



- A library of single crystal NMCs with varying compositions, sizes, and morphologies were synthesized (NMC-111, 532, 622, 631, 613, 811)
- Samples were used for systematic evaluation of facet-dependent properties
- Predicted particle shapes from modeling verified by synthesis of single crystal particles

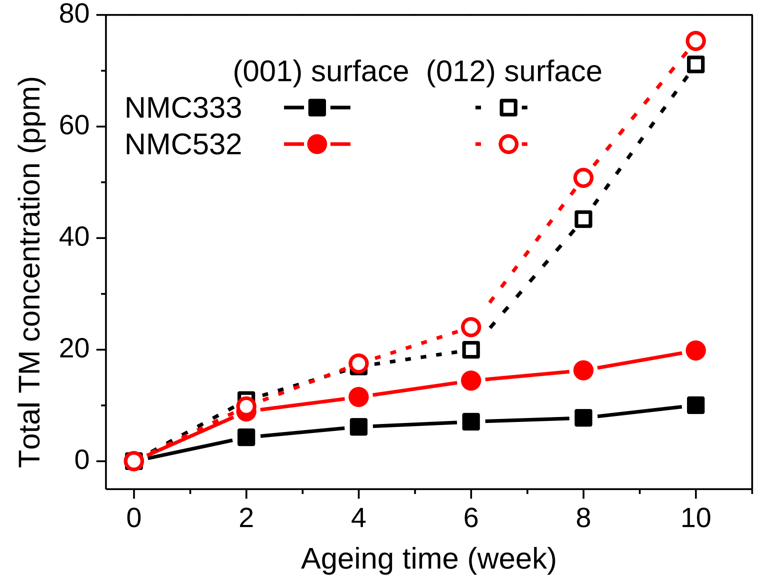
Progress: *Correlating Models, Theory and Experiment*

Theory predicts the (012) surfaces to be least stable, Co segregation to (104)



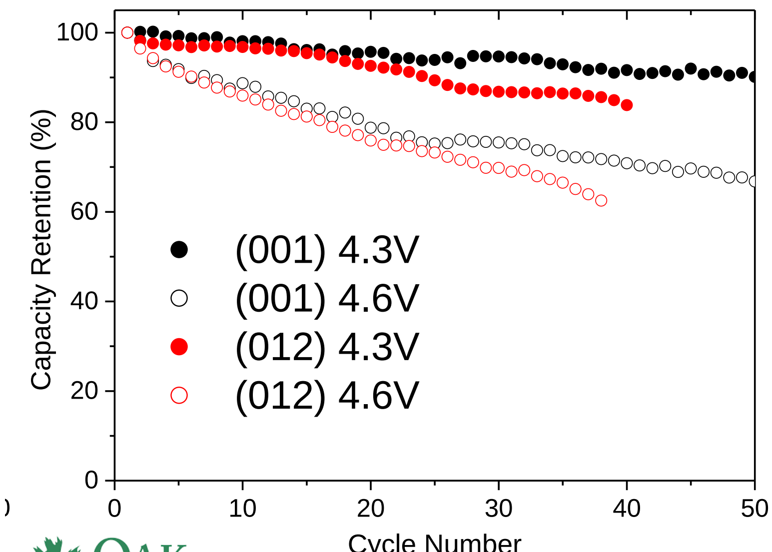
Iddir, Garcia

G. Chen et al.

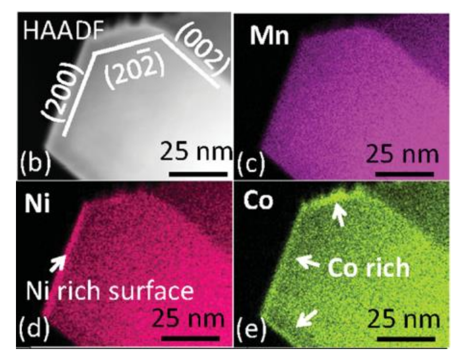


Experiment shows (012) surface has lower stability against TM dissolution than (001)

Experiment shows Co segregation to (104) surfaces



Experiment shows (012) surfaces to have lower capacity retention than (001)



Yan, P.; et. Al. *Adv. Energy Mater.* **2016**

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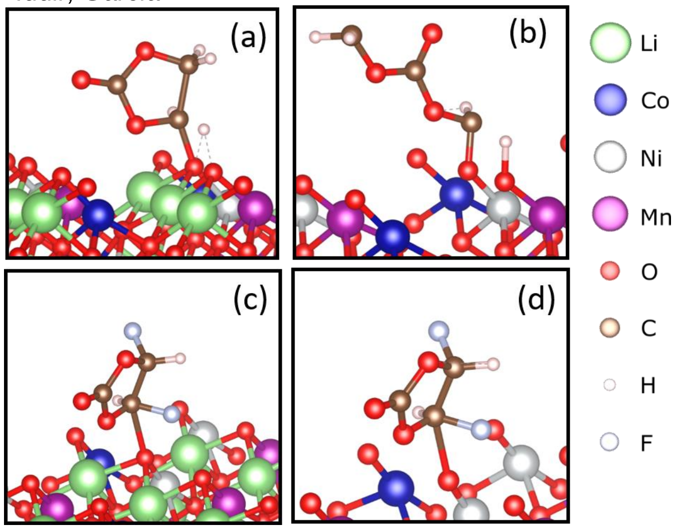
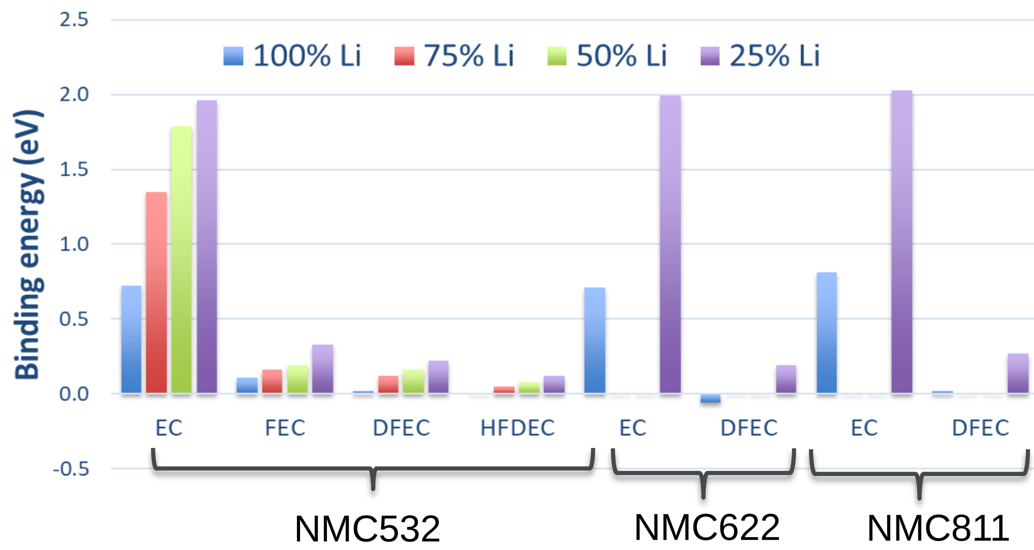
Progress: *Correlating Models, Theory and Experiment*

Iddir, Garcia

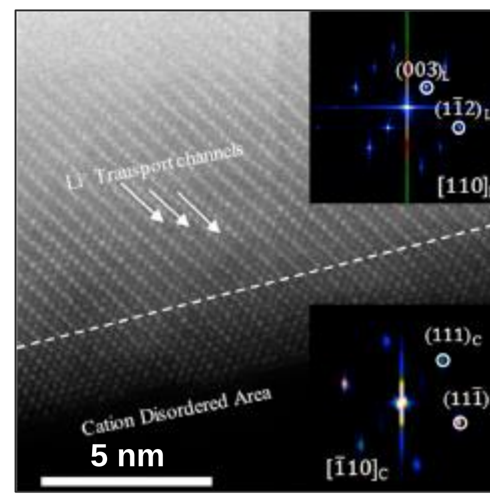




Theory predicts fluorinated electrolytes to have low reactivity with charged cathode surfaces, as compared to EC, *independent of Ni content*

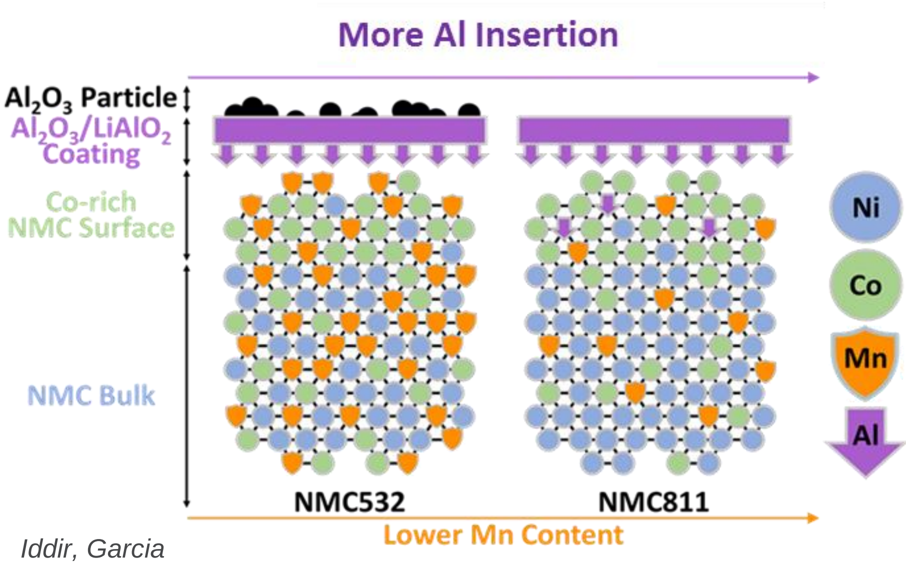
Experiment shows NMC-532 electrode exposed to 50 cycles followed by a 4.6V (Li/Li^+) hold for 100 hours has little to no surface reconstruction compared to the pristine cathode

Stability of cathode surface not only depends on composition, but is also dependent on electrolyte formulation



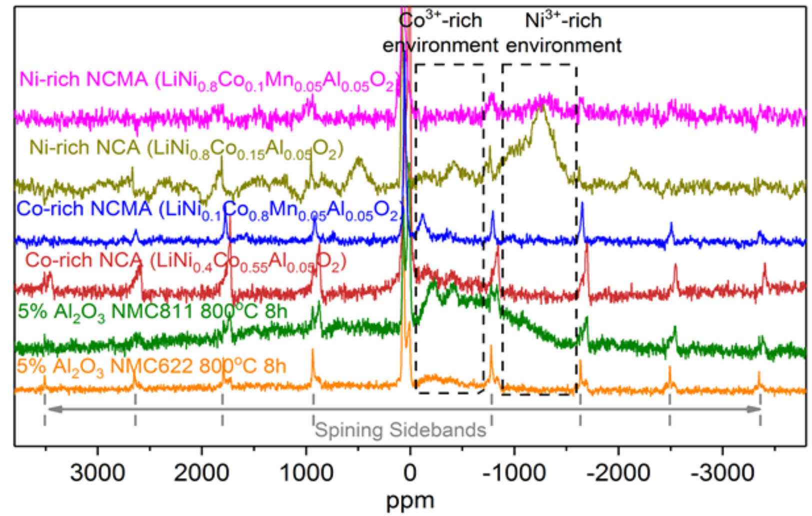
Sharifi-Asl et al.

Progress: *Correlating Models, Theory and Experiment*



Iddir, Garcia

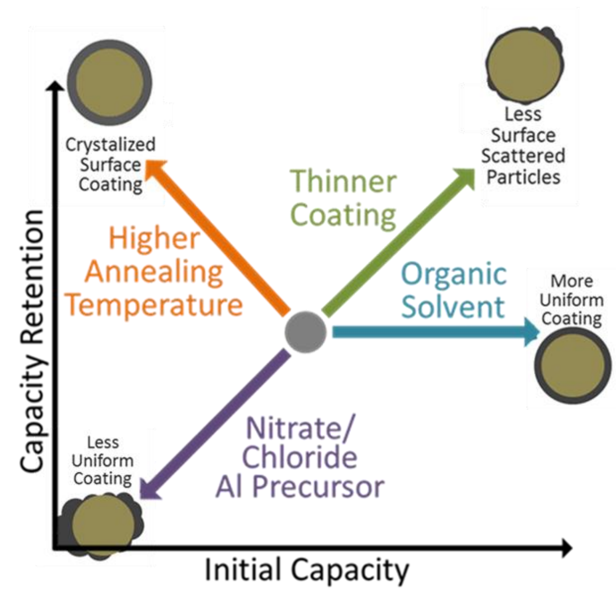
Han, Dogan, Vaughey



For high Mn content NMCs (e.g., 532), Al_2O_3 treatment leads to surface-segregated $LiAlO_2$ and/or Al_2O_3,

For high Ni content (e.g., 811) and LCO, the Al(III) is incorporated into the lattice surrounded by the TM cations

Comprehensive study of Al treatments as a function of precursors, solvents, annealing temperatures, wt%, and cathode compositions shows the complexity of even Al_2O_3-based coatings



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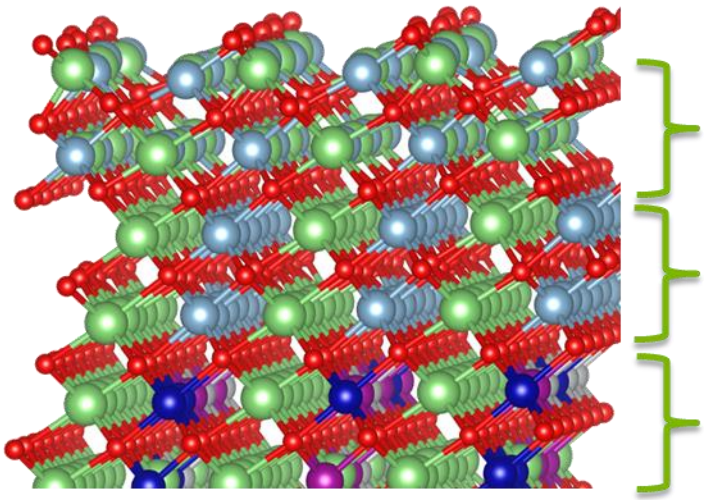
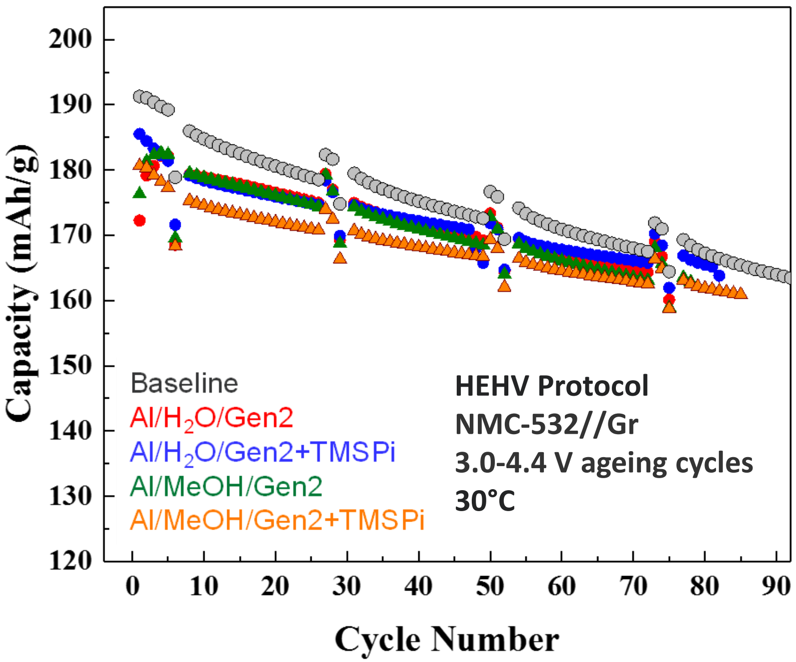
Progress: *Correlating Models, Theory and Experiment*

- α-$LiAlO_2$ / NMC interface formation energy is very low ~ 0.1eV/f.u.
- γ-$LiAlO_2$ / NMC does not form a simple interface (symmetry considerations).



Iddir, Garcia

A. Dunlop et al.



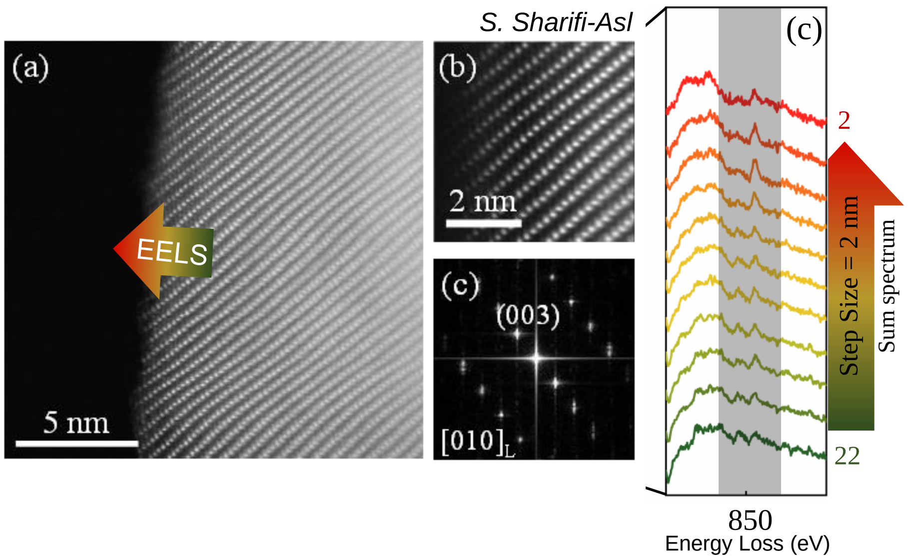
Theory corroborates complex surface interactions of Al-based coatings and NMC cathodes

No clear advantage with respect to enabling higher energy high-voltage cycling on NMCs

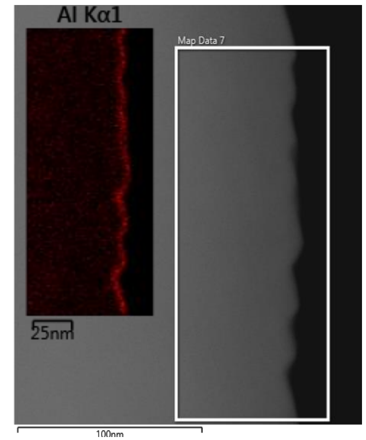
Surface treatments, even prototypical Al_2O_3-based, should be tailored to system of interest

Progress: *Correlating Models, Theory and Experiment*

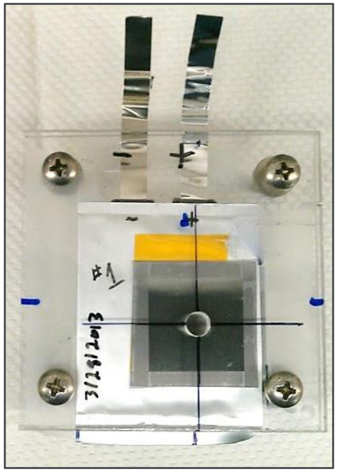
S. Sharifi-Asl

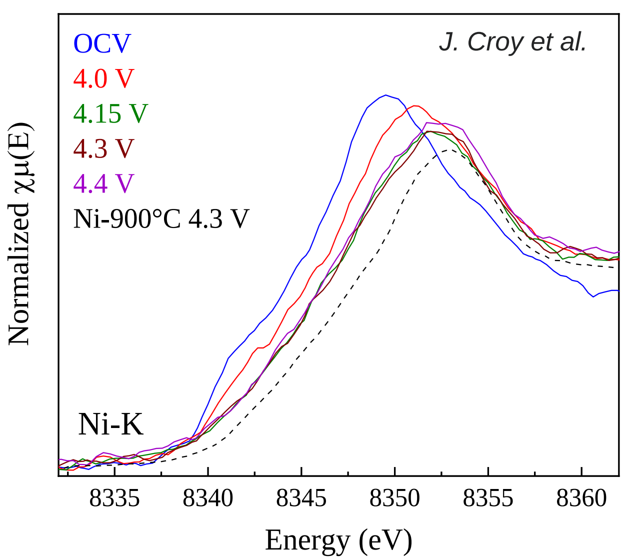


A. Mane



S. Trask





Model NMC with Ni^{2+} selectively doped into layered, R3-m environments at surface or bulk allow for hard X-ray studies

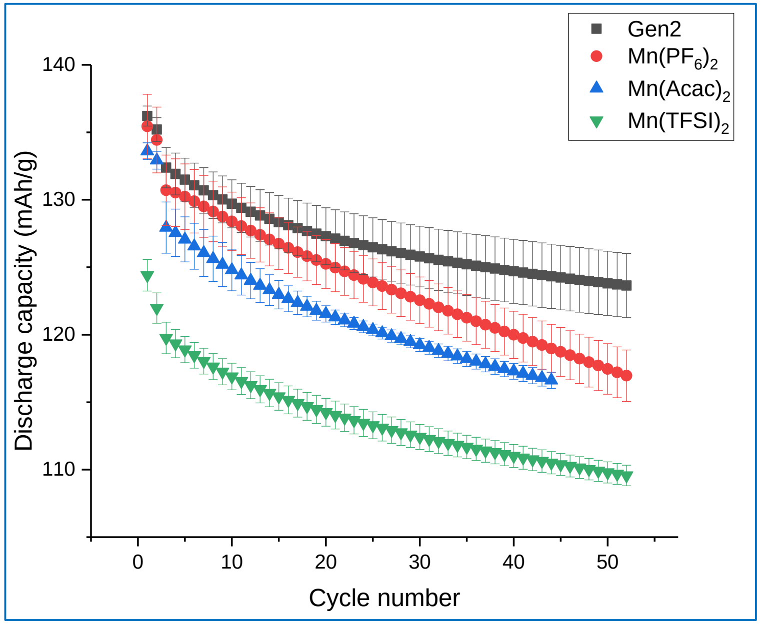
Surface $Ni^{\delta+}$ much less oxidized on charge than bulk $Ni^{\delta+}$

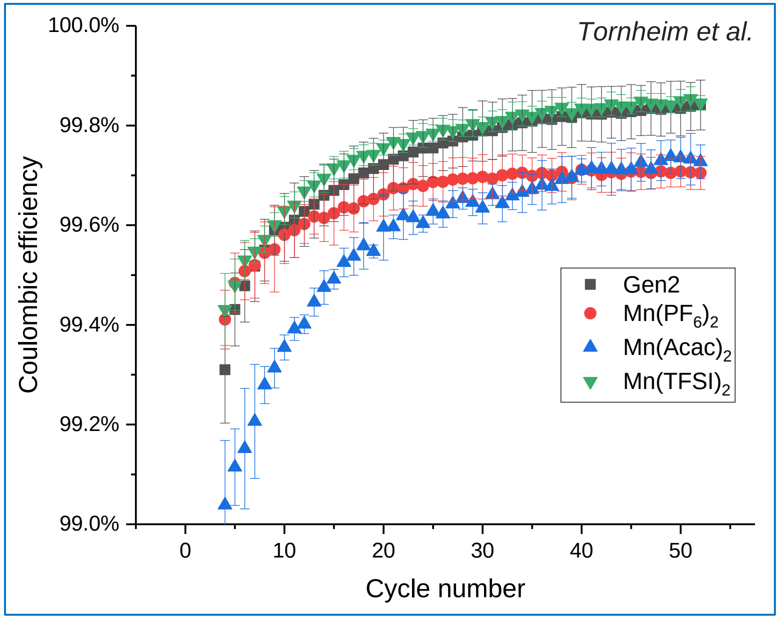
Physical barrier of Al_2O_3 (~3 nm, ALD) coating did not enable higher oxidation states of surface $Ni^{\delta+}$

Correlates well with electrochemical data and reiterates complexity of stabilizing cathode interfaces

Progress: *Development of Models, Focus on Crosstalk*

LiFePO$_4$/Gr, C/3 cycling**,** 1000 ppm Mn (by mass) in Gen2 electrolyte





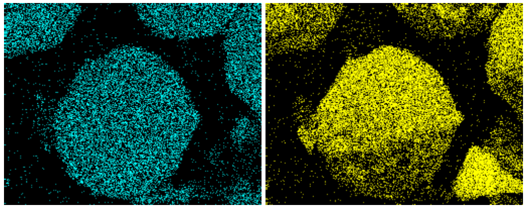
PF$_6$: Continual capacity loss
Acac: Initial and continual capacity loss
TFSI: Initial capacity loss

PF$_6$: Continual low CE
Acac: Initial and continual low CE
TFSI: No change from baseline

Cell performance is affected by the nature of the anion – coordination of dissolved species plays an important role

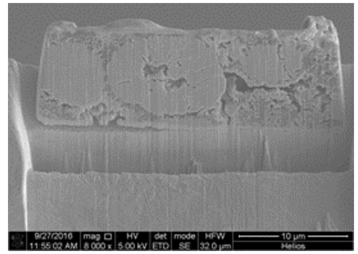
Progress: *Additional Model Examples*

Alternative Coatings



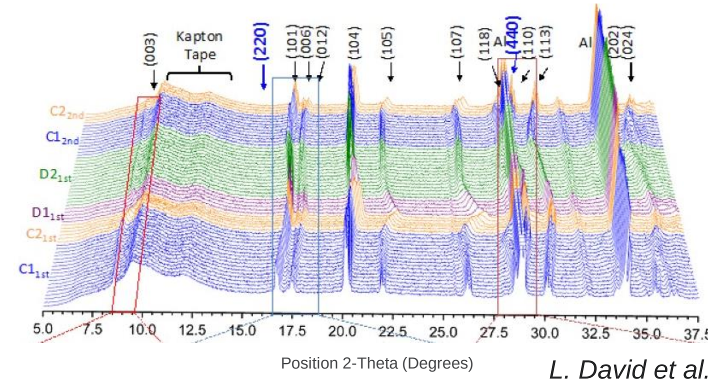
C. Peebles et al.

Microscopy



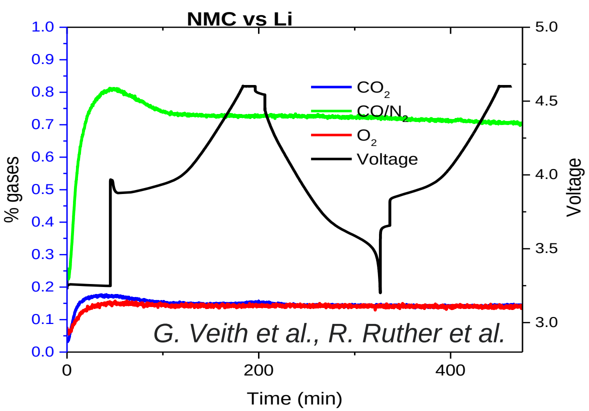
Wang et al., Shahbazian et al.

Synchrotron Studies



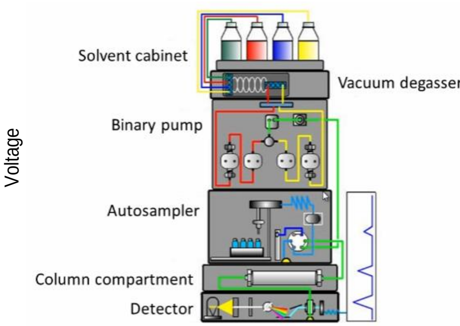
L. David et al.

Gas Evolution



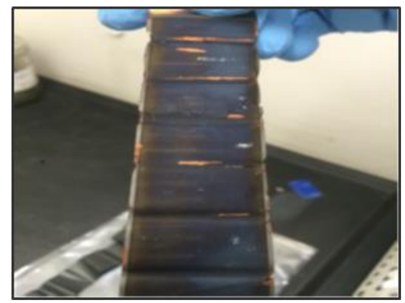
G. Veith et al., R. Ruther et al.

Chromatography



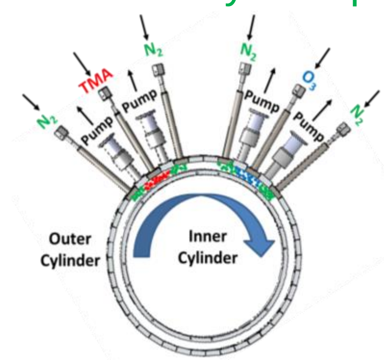
R. Sahore et al.

Post-Mortem



S. Trask et al.

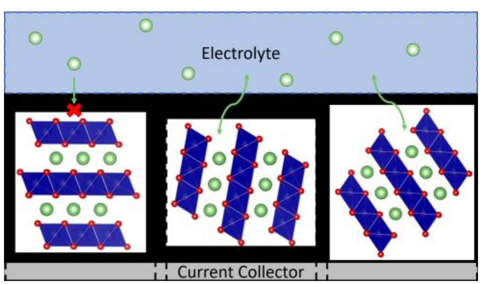
Atomic Layer Dep



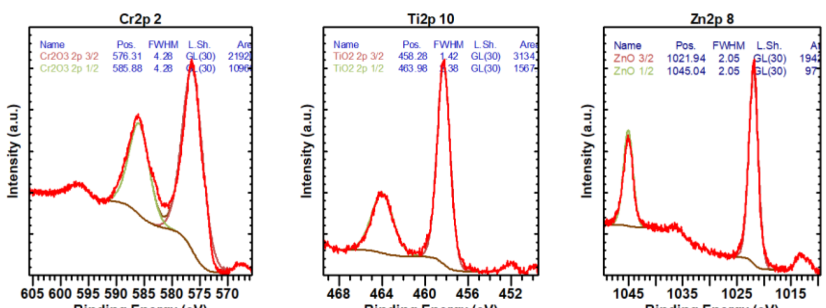
Tenent et al., Mane et al.

Thin Films

G. Veith et al.



Coated Thin Films

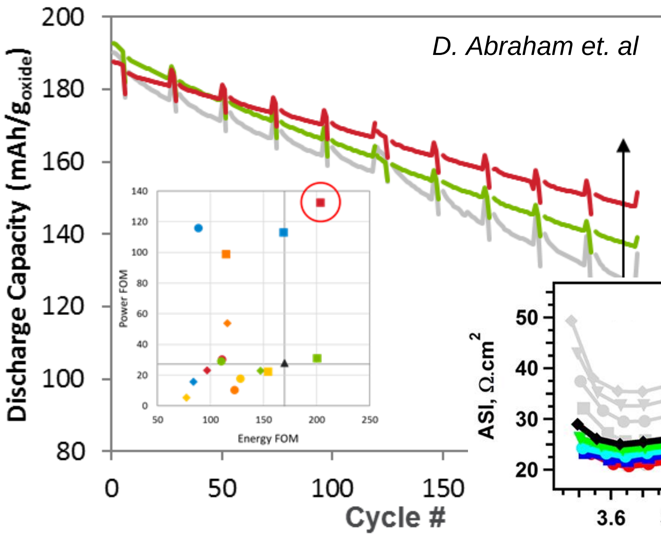


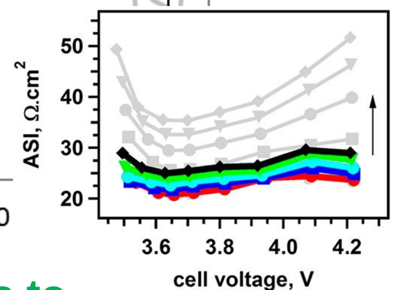
…many other efforts over the life of the project

See also BAT253

Oak Ridge National Laboratory NREL National Renewable Energy Laboratory Berkeley Lab Argonne National Laboratory

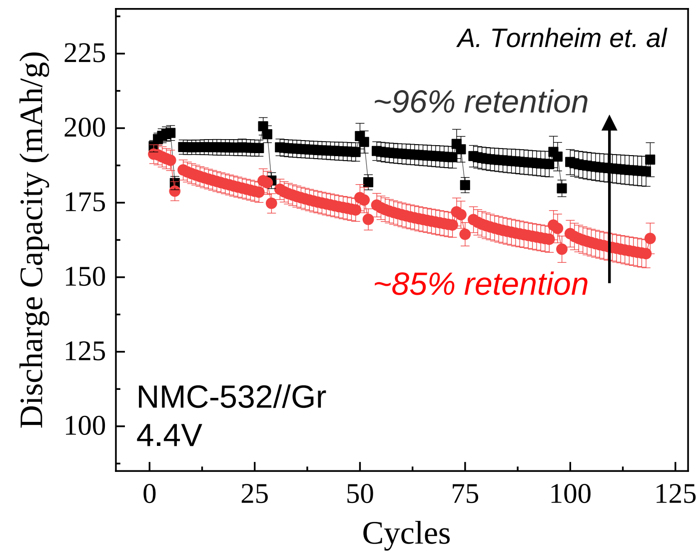
Progress: *Examples of Patented Technologies*





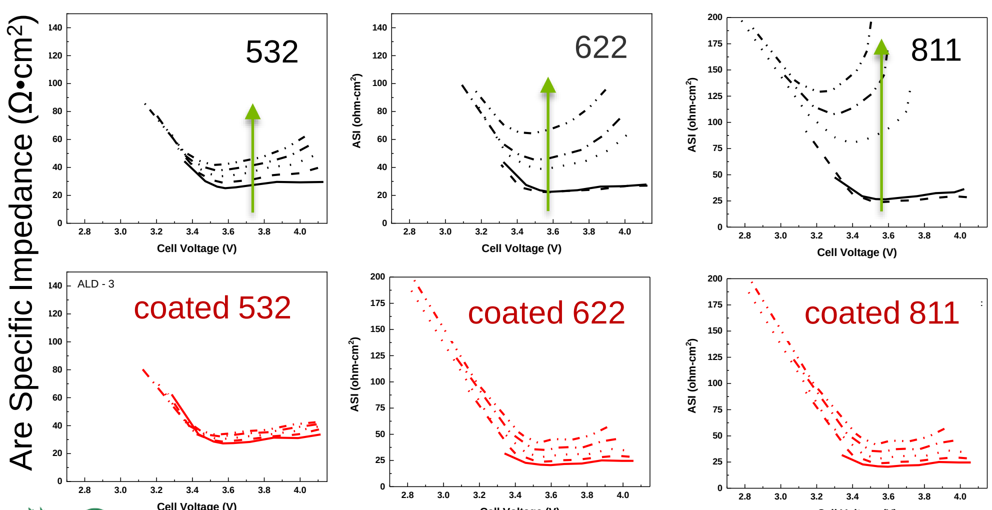
Additive design leads to

- ~20% greater energy retention
- ~50% less impedance rise, less TM dissolution



Stabilizing the graphite SEI can

- Improve capacity retention
- Lower impedance rise
- Mitigate effects of ‘cross-talk’



Novel Surface treatments

Reduce impedance rise of Ni-rich cathodes (~70% for 811)

Gutierrez et al.
(see also BAT049)

See also BAT253

Oak Ridge National Laboratory NREL National Renewable Energy Laboratory Berkeley Lab Argonne National Laboratory

Summary

- Large team working on difficult problem
  - Cathode composition/synthesis
  - Electrode/cell construction/testing
  - Confidence in reported data…

Detailed protocols w.r.t. materials and testing is a requirement for large efforts; this project has set a new standard that should/will be emulated in the future

- NMC cathode particles show facet-dependent
  - Segregation
  - Reconstruction
  - TM dissolution
  - Oxygen stability…

Strategy of combining 'practical' model systems with theory/modeling has led to mechanistic insights and experimental validation of NMC surface behavior under 'high-voltage' operation

- Stabilizing surface at high voltage involves
  - Going beyond intrinsic stabilities
  - Is not simple
  - Is system dependent…

Physical barriers are not an obvious solution, surfaces must be tailored to system of interest; theory/modeling give insights to why; crosstalk is a major issue, coordinating anions are important

- Stabilizing surface at high voltage requires
  - Continued study
  - Novel experiments
  - Is possible…

This project has shown that promising strategies exist to stabilize NMCs at higher voltages; ***NEW*** materials w.r.t. cathode surface-design and HV electrolytes/additives have been developed with positive results

See also BAT253

Future Work

- HE/HV project is officially over but the foundations built with respect to theory & modeling, model systems, standards and protocols, as well as project organization and focusing mechanisms are extremely valuable assets to have in place and major accomplishments of this team

- Important work from this program that should be followed up on/continued include detailed studies of:
  - Newly developed surface modifications
  - Newly developed electrolytes and additives
  - ***Cathode surface/bulk design and synthesis***

  - Gas generation
  - Thermal stability
  - Crosstalk

  Related to each of the above

See also BAT253

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- M. He, C. C. Su, Y. Wang, Z. Zhang, C. Peebles, Abstract, International Meeting of Lithium Batteries (2016), Chicago, IL Mechanistic Studies of Fluorinated Electrolyte for High Voltage Lithium-Ion Battery

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